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Effect of Nickel Impregnation on Wood Gasification Mechanism

Marwa Said[1,2] · Laurent Cassayre[2] · Jean-Louis Dirion[1] · Xavier Joulia[2] · Ange Nzihou[1]

Abstract To study its catalytic effect, nickel were inserted intentionally by impregnation into the biomass. In this context, the influence of the Ni amount in the solu-tion during wood impregnation has been analyzed in terms not only of catalytic activity and samples compositions but also on the wood structure. Willow was impregnated with different concentrations of nickel nitrate solutions and then characterized with thermogravimetric and elementary analyses. Using thermodynamic calculation, the speciation of Ni and the pH variation in the impregnation solution was predicted. It was found that the stable aqueous form of Ni were Ni^{2+} and $NiNO_3^+$. It was also found that wood impregnation in high-concentrated solutions (more than 0.5 wt%), modified t he w ood s tructure a nd c omplicated the understanding of its behavior during thermal treatment. The amount of Ni which shows a maximum efficiency during char gasification is 1.6 wt% in the wood sample. This amount corresponds to a sample prepared with a 0.5 wt% of Ni in the impregnation solution. However, to keep the wood structure during the impregnation step, it is recommended to impregnate the wood with lower amount of Ni, around 0.1 wt%. During gasification tests, Ni has shown a catalytic performance between 450 and 600 °C where the rate of char gasification w as i ncreasing. T his r esult w as confirmed with an increase in the syngas production. The presence of nickel has also generated a decrease in the char gasification temperature by 100 °C.

Keywords Wood · Impregnation · Nickel · Gasification · Catalytic effect

Introduction

Biomass is an important alternative energy source that can effectively be a substitute to fossil fuels. Nowadays, gasification is one of the main technologies for biomass conversion thanks to its importance for the production of fuels and synthesis gases [1]. In this frame, many researches focus on the understanding of the role and the behavior of biomass contaminants, such as heavy metals (HM), on the gasification process [2, 3]. An example of contaminated biomass is phytoextraction plants which are used to extract contaminants from polluted soils: HM accumulate inside the roots, stems and leaves of these plants [4]. For example, the concentration of zinc in crops grown on contaminated soils can reach 4650 mg/kg in contaminated willow leaves according to Lievens et al. [5]. As for Ni, Zhang et al. [6] found that some hyperaccumulators plants reach contents up to 1 mass% in their tissues.

Following the thermochemical process of biomass gasification, HM are found in the ash, gas and tar products which make them difficult to use and may increase risks to human health and the environment [3].

Regardless of the provenance of HM in the biomass, impregnation is the main technique applied in studies aiming at understanding the role and the influence of HM on the gasification process. In this context, the choice of the impregnation conditions is of high importance. Furthermore, thanks to their catalytic effect, some HM can be

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inserted intentionally into the biomass with the purpose of enhancing the thermal process by impregnation [7, 8]. With this technique, the metal is adsorbed in the biomass matrix through ion exchange with an aqueous solution containing metallic salts. Nickel, iron and cobalt are the most used HM to enhance the pyro-gasification reactions [9]. Figuereido et al. [10] have shown that nickel and cobalt have a better catalytic effect than iron. In their review of the most performing catalysts in gasification, Richardson et al. [11] confirm that Nickel (Ni) is one of the most extensively studied catalyst due to its high catalytic activity during gasification process [12, 13] and its efficiency for C–C bond rupture [14]. In most of the studies devoted to Ni catalytic effect during thermal treatment, wood samples are impregnated in solutions containing high concentrations of metallic salt (0.3 until 1 mol/L) [15, 16]. However, to our knowledge, there are no works published specifying the metal concentration range that should be used to only notice the catalytic effect of the metal. Indeed, as it will be developed in this work, the wood structure can be damaged during the impregnation protocol, which is of high importance in the view of understanding the role of HM in gasification of contaminated biomass.

Thus, the present study aims to define the adequate impregnation conditions to understand the catalytic effect of Ni during wood gasification without modifying the wood structure. For this purpose, elementary and thermogravimetric analysis were carried out for willow samples that were impregnated in aqueous solutions with various concentrations of nickel (from 0.01 to 5 wt% Ni). The speciation of Ni in the impregnation solutions were predicted with thermodynamic calculations. The catalytic effect of Ni was also characterized with gasification experiments in a fixed bed reactor and subsequent analysis of the gas composition.

Materials and Methods

Sample Preparation

Willow obtained from 'pépinières-Naudet' company (France) was used in this study. The pellets were dried, crushed and sieved to a range of particle size of 0.5–1 mm. 30 g of willow wood particles were then impregnated with 300 mL of nickel nitrate aqueous solution prepared with $Ni(NO_3)_2{\cdot}6H_2O$ (Sigma–Aldrich, 99% purity). Nitrates compounds were selected as they do not contain carbon atoms. The obtained mixtures were stirred at ambient temperature. Two different procedures were applied for the impregnation of wood samples. For the first one, the samples were impregnated for 72 h with nickel concentrations in the solutions of 1.3 and 5 wt% of Ni. For the second one, samples were prepared using lower Ni concentrations (0.01, 0.05, 0.07, 0.1 and 0.5 wt%) and shorter impregnation times (24 h). The wood particles were then filtered and dried at 60 °C for 24 h. In the following, the samples are labelled wood-X-Ni, X being the Ni concentration in the impregnation solution. Raw-wood corresponds to a non-impregnated wood.

Characterization Techniques

In order to assess the effects of wood impregnation on the final wood chemical composition, analyses of the Ni, C, H, O and N content, as well as the main alkali metals were performed.

Elemental Analysis

The chemical composition of wood in terms of C, H and N was determined by an elemental analyzer CHNO- Flash 2000. The wood was combusted at 950 °C in an excess of oxygen for a complete combustion. The emitted quantities of CO_2, NO_2, and H_2O were determined by gas chromatography coupled to a thermal conductivity detector (TCD). As for the oxygen content, the same method was used but in this case the sample was pyrolysed at 1070 °C under helium atmosphere and the emitted gas was CO.

Mineralization Protocol

A specific mineralization protocol was developed in order to perform the inductively coupled plasma optical spectroscopy (ICP-OES) analyses. For this purpose, 200 mg of sample were immersed in 10 mL of an oxygenated water and nitric acid solution. The mixture was put first in a special fluoroplastic flask (PTFE) then in a pressure digestion vessel made of high alloy stainless steel SS 316 Ti (DAB-2). The vessel was then put in an electric heating block for 4 h at 200 °C under high pressure (max 200 bar).

Visual inspection of the resulting solutions showed the absence of any solid residue. The solutions were then diluted and analyzed by ICP-OES (HORIBA Jobin Yvon ULTIMA-2) in order to quantify the amount of inorganic species. The filtrated impregnation solutions were also analysed to quantify the remaining amount of the nickel. The combination of wood and solution analyzes lead to a satisfactory Ni mass balance (4%).

Micro-GC

The gases produced in the fixed bed reactor (see Section "Influence of Ni content on CO and H2 production in fixed bed reactor") were collected in 0.5 L sampling bags. Samples were analyzed by gas chromatograph (My-GC

from SRA Instruments) equipped with two analytical columns and TCD. N_2, O_2, H_2, CO and CH_4 were analyzed on a Molsieve 5 A column and CO_2, C_2H_4 and C_2H_6 on a Poraplot Q column. For each compound, a calibration using reference gases at three different concentrations was done. Three measurements were performed for each experiment leading to a satisfactory repeatability (error = 1%).

Thermogravimetric Experiments

Thermogravimetric analysis (TGA) was performed under atmospheric pressure using a TGA/DTA analyzer (SDT Q600) to determine the effect of wood impregnation in the mass loss. 10–17 mg of sample was placed in platinum crucibles and heated from room temperature to 1000 °C with a rate of 5 °C/min. All analyses were made under mixed atmospheres of N_2 (2 L/h) and CO_2 (6 L/h). Each TGA was repeated at least three times and the mean standard deviation of weight loss was lower than 1%.

Gasification Experiments

The tests were performed in a quartz tube fixed-bed reactor. A schematic diagram is presented in Fig. 1. A sintered quartz disk was placed inside the reactor to support the wood samples. For all the experiments, the heating rate was at 5 °C/min. Before the gasification tests the wood samples were pyrolysed under N_2 flow (100 mL/min) up to 450 °C. An isotherm of 1 h was done at 450 °C. Gas samples were taken at the beginning, middle, and end of the isotherm and analyzed in order to evaluate the progress of the pyrolysis reactions. Gasification tests were then carried out under mixed atmosphere (90 mL/min of CO_2 and 12 mL/min of N_2) from 450 to 950 °C. The sample was then maintained for 1 h at 950 °C. After cooling down to room temperature, the samples were finally collected, weighted and analyzed. During the reaction, gas products were collected in 0.5 L bags, and analyzed using a μ-GC. Between 500 and 900 °C, the gas is collected during 5 min at each 100 °C. For the isotherm (at 950 °C), the gas is also collected during 5 min at the beginning, the middle and the end of the isotherm.

Thermodynamic Calculations

On top of pH measurement, two thermodynamic models were used to compute the pH variation of the impregnation solutions, using the Phreeqc software [17]. The first model, which is a variant of the Debye-Hückel model available in the Lawrence Livermore National Laboratory database database (LLNL), is considered to be valid up to ionic strength of about 0.5 mol/L. The second model, based on the specific ion interaction theory and available in the Specific ion Interaction Theory database database (SIT), is accurate at higher ionic strength (typically from 0.1 to 6 mol/L).

Results and Discussion

Solution pH and Speciation

As reported in Fig. 2, the measured pH of the impregnation solutions strongly decreases with increasing nickel nitrate concentration. Indeed, from about 6.8 at low Ni content, pH drops to 5.0 for the solution containing 5 wt% Ni. The LLNL model is indeed reproducing correctly the pH variation of the $Ni(NO_3)_2$ solutions at low salt concentrations (and thus at low ionic strengths), while SIT model is more adapted at high salt concentrations.

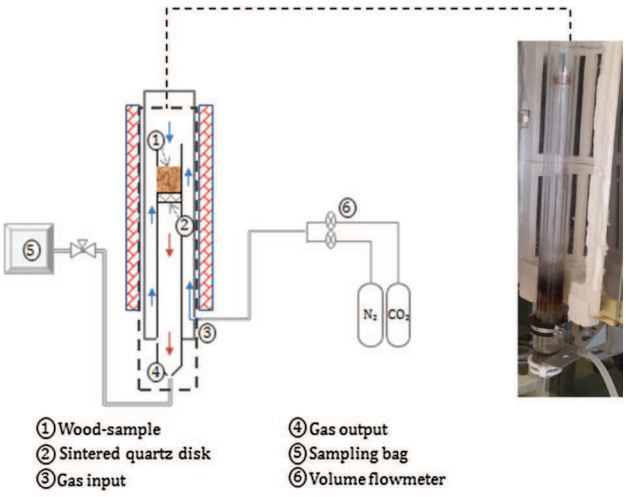


Fig. 1 Fixed bed Reactor

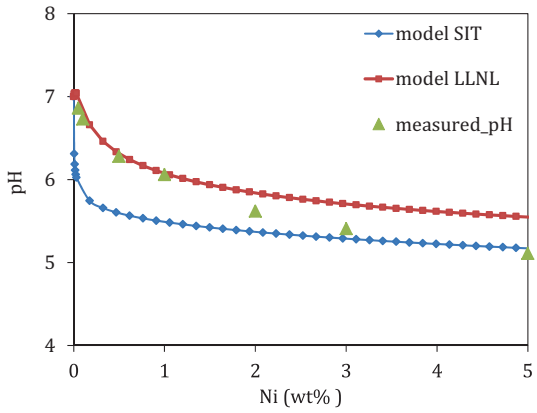


Fig. 2 Measured and calculated (according to two different models) pH variation of the nickel nitrate solutions at 25 °C

According to these models, the nature of the ionic nickel species in the aqueous solution depends on the pH values and consequently on the Ni concentration. Figures 3 and 4 present the computed speciation of Ni in the solutions for low and high concentrations, using LLNL and SIT models respectively. At very low concentrations (Fig. 3), Ni is mainly present in solution in the form of Ni^{2+} cations. At a concentration of 1 wt% Ni, the ion proportion is approximately 80% Ni^{2+} and 20% $NiNO_3^+$. In the case of high concentration of Ni (Fig. 4), the amount of $NiNO_3^+$ progressively increases and reaches 50%. As for the speciation of Ni, calculations show that NO_3^- and $NiNO_3^+$ are the only stable species.

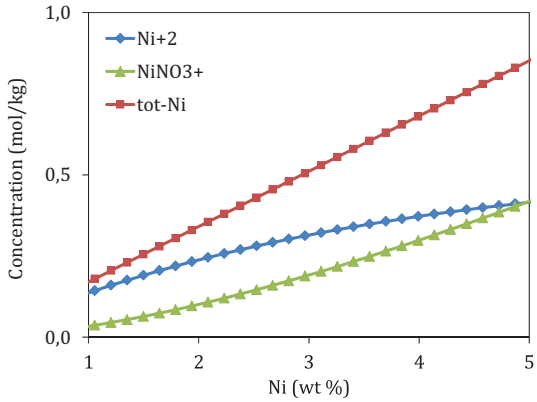


Fig. 4 Speciation of Ni using SIT model

Impregnated Wood Characterization

Tables 1 and 2 show respectively the elemental analysis results and the concentrations of the main alkali and alkaline earth metals of wood samples before and after impregnation with the nickel nitrate aqueous solutions. For the samples impregnated for 24 h at low concentrations of nickel (less than 0.5 wt%), the amounts of the alkali and alkaline earth metallic species slightly decrease. Those species are replaced during impregnation by the Ni species. No significant modifications are observed for the amounts of C, H, N and O compared to the raw-wood. However, the sum of the major elements is less than 100% (Table 1) for the samples impregnated in high concentrations of Ni. This difference is due to the fact that the percentage of oxygen measured in the elemental analysis does not take into account the percentage of oxygen remaining as NiO. The increase of both the metal concentration in the impregnation solution and the time of impregnation (3 days) for the wood-1-Ni, wood-3-Ni and wood-5-Ni, increase the inserted amount of Ni in the wood. However, it provokes many modifications in the elemental and chemical wood compositions. The decrease of the hydrogen and carbon contents could be attributed to the loss of organic extractible and the ion-exchange between the nickel and the wood compounds. Indeed, many complex reactions between phenolic groups (lignin), glucuronic acid (cellulose) and metallic ionic species takes place during impregnation [18, 19]. Besides, lignin C–O bond might be involved in metal uptake as proved by Villaescusa et al. [20].

The increase in oxygen and nitrogen content is attributed respectively to the adsorption of hydrated nickel species and nickel nitrate $NiNO_3^+$ [15]. The considerable loss of alkali can be explained by an exchange mechanism between nickel and alkali and alkaline earth metallic species as explained by Degroot et al. [18].

It was also reported in the literature that adding wood to a nickel nitrate solution led to a pH decrease [8]. Furthermore, other authors [21, 22] have reported that at low values of pH, wood samples are washed, which means that they lose some of their minerals. In the specific case of this work, the washing of willow at high Ni concentrations is clearly highlighted by the analyses presented in Table 2. Degroot et al. study [18] was focused on the understanding

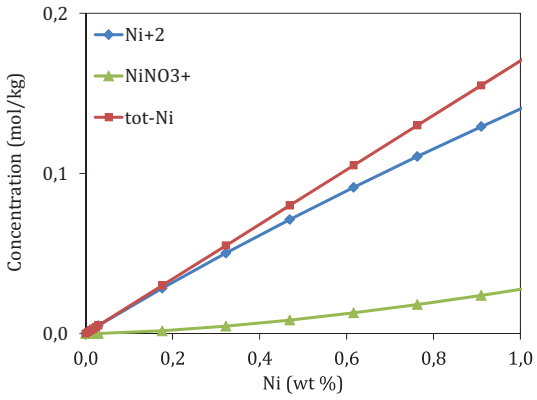


Fig. 3 Speciation of Ni using LLNL model

Table 1 Elementary composition of the impregnated samples and raw wood

Samples	Concentration (wt%)				
	Ni	C	H	N	O
Raw-wood	–	48.8	5.9	0.6	43.8
Wood-0.01-Ni	0.09	48.9	5.9	0.7	43.6
Wood-0.05-Ni	0.34	48.7	5.8	0.7	43.9
Wood-0.07-Ni	0.48	47.6	5.7	0.7	44.4
Wood-0.1-Ni	0.55	47.0	5.6	0.7	44.2
Wood-0.5-Ni	1.60	46.7	5.5	1.1	44.6
Wood-1-Ni	2.14	42.0	5.4	1.4	46.2
Wood-3-Ni	5.57	29.5	4.5	4.3	49.4
wood-5-Ni	8.45	26.5	4.4	4.4	50.9

Table 2 Influence of the wood impregnation treatments on the concentrations of the main alkali metals

Samples	Concentration (mg/kg)				
	Ca	K	Mg	Na	P
Raw-wood	4255.4	847.1	275.1	167.6	451.0
Wood-0.01-Ni	4079.8	747.6	187.6	120.2	324.8
Wood-0.05-Ni	4172.1	698.7	173.5	149.4	343.1
Wood-0.07-Ni	4125.9	764.7	163.4	134.8	345.4
Wood-0.1-Ni	3071.7	673.6	128.4	113.1	322.0
Wood-0.5-Ni	2958.0	665.1	128.3	125.8	314.3
Wood-1-Ni	1798.7	437.53	72.9	72.9	243.0
Wood-3-Ni	1544.8	465.9	73.5	73.5	294.2
Wood-5-Ni	911.7	369.6	49.3	73.9	246.4

of the metal-wood impregnation mechanism. They showed that the acidity of the solutions attacks the wood structure and decomposes the mean compounds of wood: cellulose, hemicellulose and lignin. The compounds of those polymers, such as the glucose, react with the metallic ions and form a metal complex. The analyses compiled in Table 1 clearly indicate that the wood structure was attacked by the highly concentrated Ni solutions.

The Scanning Electron Microscopy (SEM) images of the raw-wood and wood-5-Ni sample are depicted in Fig. 5. It can be seen that the Ni particles are deposited on the surface of the wood. The second important difference between the raw-wood and the impregnated sample is that the wood structure was strongly modified after the impregnation, which is in agreement with the elementary analysis.

TG Characterization of the Thermal Decomposition of Impregnated Woods

Thermal analysis was used to study the thermal decomposition of raw and impregnated wood samples. Two types of data are presented in this section: the weight variation of the sample as a function of temperature (TG) and the derivatives of TG curves (DTG). The DTG peaks correspond to the inflexion points of TG-curves. These curves allow a precise understanding of the thermal processes within the sample.

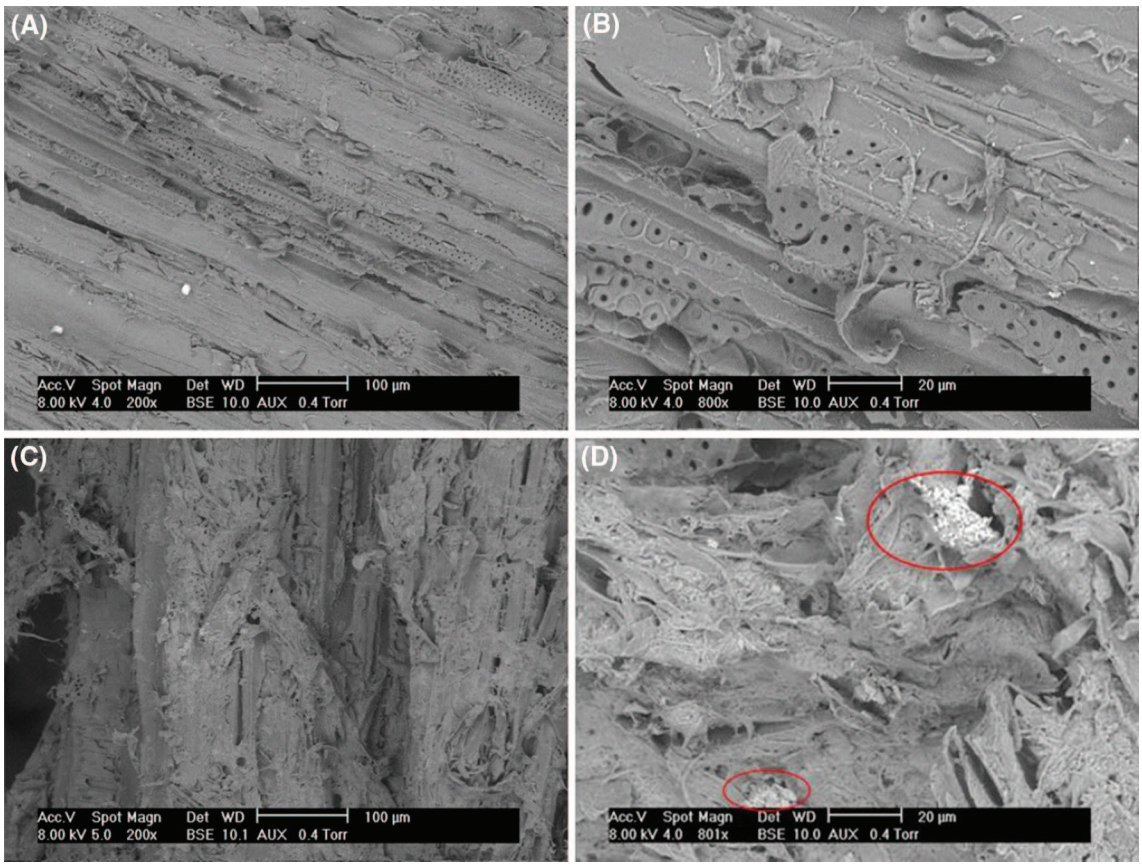


Fig. 5 SEM images of raw wood (**A, B**) and the wood-5-Ni sample (**C, D**)

Effect of High Concentrations of Ni

Figure 6 shows the TG curves of raw-wood and of three samples impregnated at high concentrations of nickel nitrate during 3 days. As already well described in the literature [23], the TG profile of raw wood exhibits three distinct phases, corresponding to water evaporation (zone A), main pyrolysis (zone B) and gasification (zone C). The main mass loss occurs in the pyrolysis region (zone B), which proceeds from 200 to 650 °C. At this stage, the hemicellulose and cellulose compounds of wood are decomposed. At a temperature beyond 350 °C, the mass loss is mainly due to a slow degradation of lignin and the release of the remaining volatiles from the wood sample [24]. The final mass loss of the TG curve (zone C) is due to the char gasification.

Figure 6 shows that the TG curves of impregnated samples vary significantly comparing to the TG of raw wood. The pyrolysis starts earlier (around 150 °C) showing the impact of the nickel impregnation, specifically for the wood-3-Ni and wood-5-Ni samples. Many studies [15, 25] explain this modification by a catalytic effect of Ni in the hemicellulose, cellulose and lignin decomposition during pyrolysis.

In fact, those changes are not only caused by a catalytic effect of Ni on hemicellulose and cellulose decomposition. When the Ni concentration increases, the percentage of nitrate in the samples also increases. As it was explained in the previous section, for the impregnated samples in a high concentration of Ni, the half of the adsorbed Ni species in the wood samples is $NiNO_3^+$ (Fig. 3). In order to take into account only the wood decomposition, the mass loss caused by the nickel nitrate degradation has been subtracted from the experimental mass loss curves. For this calculation, the percentage of mass loss due to the nickel nitrate decomposition (Fig. 7) present in the sample has been subtracted from the total mass loss of the wood-5-Ni sample. Figure 8 presents the

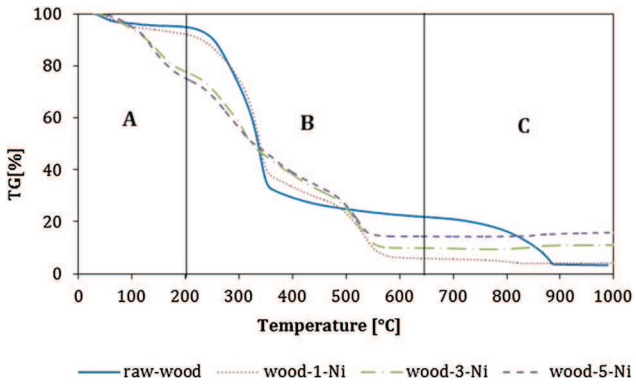


Fig. 6 TG profiles of wood samples impregnated during 3 days

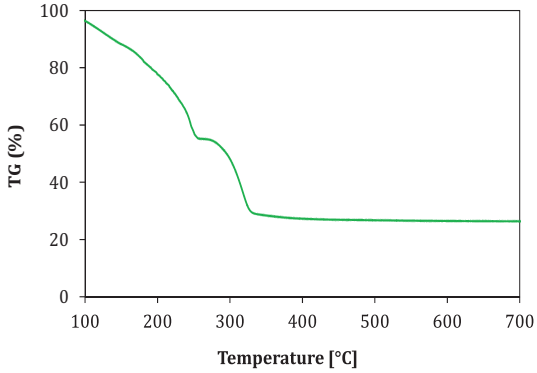


Fig. 7 Nickel nitrate degradation at 5 °C/min

TG profiles for the samples without taking account of the mass loss due to nitrate decomposition (wood-5-Ni_cor) and the TG profile of the wood-5-Ni sample. It shows that the decomposition of nickel nitrate added to the wood-5-Ni sample has no major influence on the total mass loss of impregnated wood.

Moreover, as shown in Fig. 6 (zone B), at a temperature above 600 °C, no mass loss is detected for the three impregnated samples. Therefore, it can be concluded that not only the degradation of nickel nitrate, hemicellulose, cellulose, and lignin occurred between 100 and 600 °C but also the char gasification which is catalyzed by the presence of Ni. The difference between the TG profiles of the treated wood samples (Fig. 6) during the gasification is mainly attributable to the decrease of the amounts of cellulose, hemicellulose and especially lignin comparing to the raw wood. In fact impregnating wood in nickel nitrate aqueous solutions at low pH during 3 days probably caused the deterioration of wood structure (Table 1).

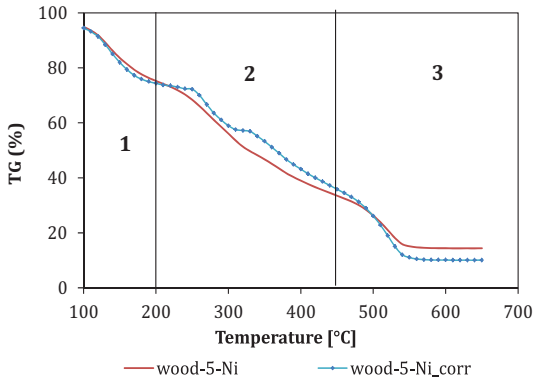


Fig. 8 TG profiles for wood-5-Ni with and without the decomposition of nickel nitrate

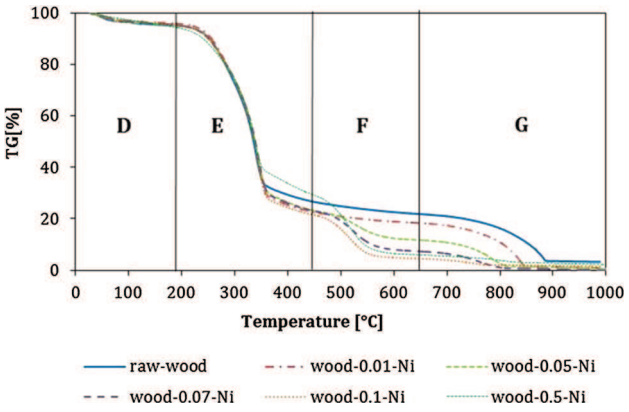


Fig. 9 TG profiles for wood samples impregnated during 24 h

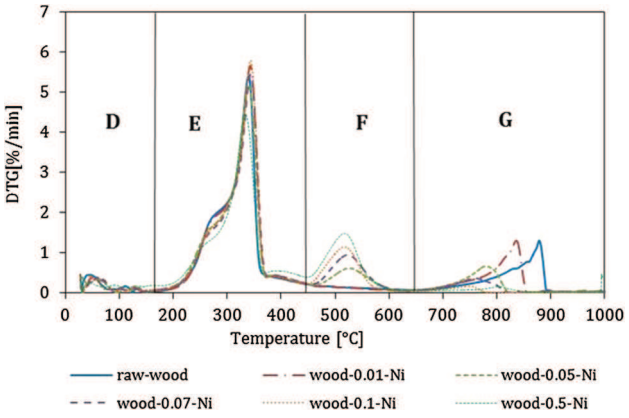


Fig. 10 DTG profiles of impregnated wood samples during 24 h

Concentration Threshold on the Catalytic Effect of Ni

The TG and DTG profiles of impregnated samples in 0.01, 0.05, 0.07, 0.1 and 0.5 wt% of nickel in the aqueous solutions during 24 h are presented respectively in Figs. 9 and 10. For the wood-0.5-Ni sample, the TG and DTG profiles (zone E) show a different behavior comparing to the other profiles and are similar to the one of wood-1-Ni sample (Fig. 6). As previously explained, at these high concentrations of Ni the separation between the impregnation effect and the catalytic effect of Ni on the thermal degradation of wood are not possible. For the other samples (wood-0.01-Ni, wood-0.05-Ni, wood-0.07-Ni, wood-0.1-Ni), the TG curves are perfectly overlaid until 350 °C with the raw-wood curve. That allows an easier analysis and understanding of the modifications introduced by the presence of Ni during the gasification reaction.

The slight shift of 4% in the mass loss observed at 350 °C between the TG curve of raw wood and the curves of treated wood is likely due to the fact that the wood structure was partially damaged during the impregnation step. Even at very low concentrations of nitrate (wood-0.01-Ni), wood was partially attacked by the acid solution. Moreover, ion-exchange between the polymer and the Ni particle probably occurred.

The DTG profiles of the samples (Fig. 10, zone E) reveal an intense peak at about 350 °C, which is attributed to hemicellulose and cellulose decomposition. The last peaks correspond to the char gasification reaction, which occurs at around 890 °C for the raw-wood sample. As it can be seen in Fig. 10 (zone G), the presence of Ni decreases the char gasification temperature to 840 °C for wood-0.01-Ni, 790 °C for wood-0.05-Ni and around 750 °C for wood-0.07-Ni and wood-0.1-Ni samples.

For all the impregnated samples, except wood-0.01-Ni, new peaks appear between 450 and 600 °C (zone F) which are more intense for higher Ni concentrations. These peaks correspond to a catalytic effect of Ni on the gasification reaction (Eq. 1). A possible explanation is that the initial concentration of Ni in the wood-0.01-Ni sample was too small for any effect to be observe on the DTG curves around 500 °C. Indeed, the catalytic activity of Ni during gasification increases char gasification rate which causes a shift in the DTG curve towards lower temperatures.

As showed by the modeling of the speciation of the aqueous solution (Figs. 3, 4), Ni is found as Ni^{2+} or $NiNO_3^+$ cations in the solution, depending on the initial concentration of Ni in the impregnation solution. During the impregnated samples gasification, $Ni(NO_3)_2$ is decomposed to form a nickel oxide (NiO) around 350 °C. However, several works [10, 22] showed that Ni is an active catalyst only under its metallic form Ni^0. In fact, the Ni^{2+} particles are reduced between 450 and 600 °C to nanoparticles Ni^0 by the amorphous carbons (Eq. 2) [26, 27]. Those nanoparticles are incorporated as a complex into the carbon structure and form active sites for the gasification reaction. The production of H_2 in this range of temperature (Fig. 13) could also participate in the reduction of nickel oxide as presented in Eq. (3) [28].

$$CH_\alpha O_\beta + (1-\beta)\,CO_2 \rightarrow (2-\beta)\,CO + \frac{\alpha}{2}\,H_2 \quad (1)$$

$$NiO + C \rightarrow Ni^0 + CO \quad (2)$$

$$NiO + H_2 \rightarrow Ni^0 + H_2O \quad (3)$$

The catalytic performance of Ni not only depends on the reaction atmosphere but also on the catalyst amount. Figure 11 shows the intensity of the TDG peaks at 520 °C as a function of the Ni amount in all the impregnated samples. It clearly illustrates the catalytic effect of Ni, which increases significantly with the number of active sites of Ni in the samples. Above a concentration of 1.6 wt% of Ni in the wood which corresponds to the wood-0.5-Ni sample,

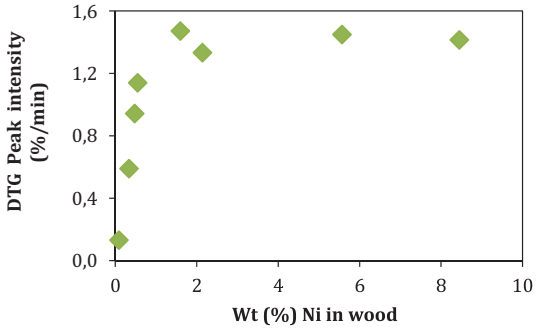


Fig. 11 Effect of the concentration of Ni on its catalytic effect at 520 °C

the increasing of the Ni amount has no influence on the char gasification rate.

The curve presents a saturation effect of Ni regarding its catalytic effect. So it can be concluded that the amount of Ni which shows a maximum efficiency during char gasification is 1.6 wt% in the wood sample. This amount corresponds to a sample prepared with a 0.5 wt% of Ni in the impregnation solution. However, to keep the wood structure during impregnation step, it is recommended to impregnate the wood in a lower amount of Ni, around 0.1 wt%.

Influence of Ni Content on CO and H_2 Production in Fixed Bed Reactor

Figures 12 and 13 show the productivity of CO and H_2 during gasification experiments in a fixed bed reactor of the raw-wood and the impregnated woods, respectively. The X axis corresponds to the sampling temperature and also the sampling time during the isotherm for the last three points. For raw-wood, the H_2 is detected in an important production value until 950 °C and the CO production reaches its

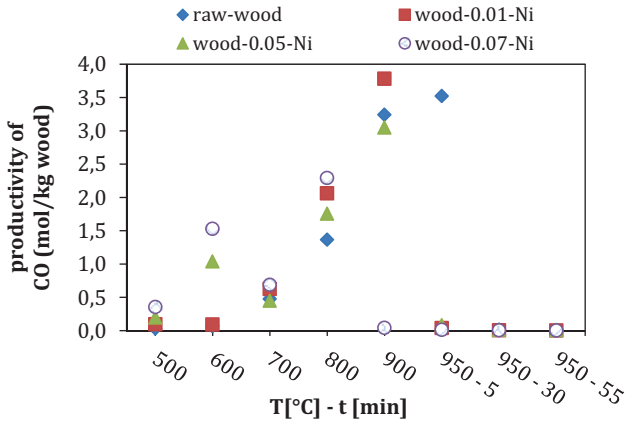


Fig. 12 Yield of CO production for all the samples

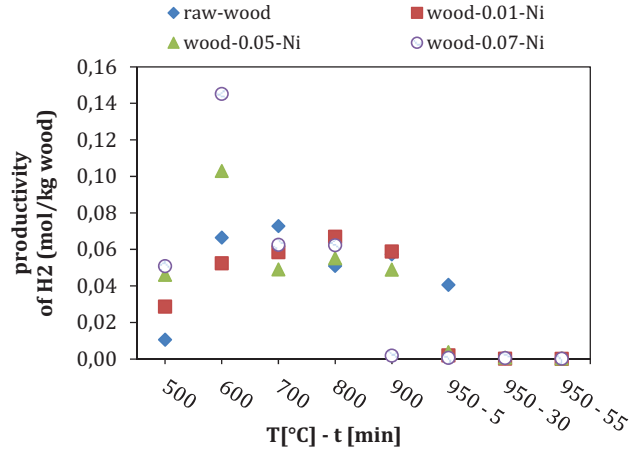


Fig. 13 Yield of H_2 production for all the samples

maximum (71%) between 900 and 950 °C. However, for all the samples containing Ni, no CO and H_2 are detected at 950 °C; not even at 900 °C for wood-0.07-Ni sample, which means the ending of the gasification reaction. The presence of Ni in gasification experiments involves a significant increase in the CO and H_2 production between 500 and 600 °C for both wood-0.05-Ni and wood-0.07-Ni samples, which is in good accordance with TG-DTG data and their interpretations. It confirms that the increase of the syngas production between 500 and 600 °C is due to the activation of in site Ni^0 nanoparticles as established by Richardson et al. [15]. The difference of Ni activation temperature between the TG and the gas analysis results is most likely due to the scale change between the two experiements. Indeed, the gasification experiments in the fixed bed reactor were done with 5 g of each sample while the TGA were performed with 15 mg. The scale change between the two experiences influence even the temperature of the gasification experiment using a raw wood where during TGA experiences the gasification reactions end at 900 °C while in the fixed bed reactor it end at 950 °C.

Conclusions

The first aim of this study was to investigate the influence of wood impregnation protocol on pyrolysis and gasification process in order to avoid side effects such as wood structure degradation. Then, the impregnation conditions adapted to the study of the catalytic effect of Ni were clearly defined. It has also been shown that metal impregnation is a key step to understand its implication in the biomass gasification mechanism. The combination of thermodynamic calculations, thermogravimetric and elementary analysis has shown that wood impregnation in a range of nickel concentration between 0.5 and 5 wt% strongly modifies the wood

structure and composition and consequently its behavior during thermal treatment. Additional studies, as for example the analysis of the amount of cellulose, hemicellulose and lignin before and after impregnation, should be conducted to better understand the interactions between the metal and the wood.

This study has shown that 1.6 wt% corresponds to the amount of Ni which provides a maximum efficiency during char gasification. This corresponds to a concentration of 0.5% of Ni in the impregnation solution. However, to preserve the wood structure during impregnation step, it is recommended to use a nickel concentration in solution of maximum 0.1 wt%. The wood concentrations of nickel obtained through impregnation in less than 0.1 wt% are similar to those usually found in the literature for phytoextraction plants grown on contaminated soils, since the Ni contents can vary in those plants between 1 wt% [6] and 0.1 wt% [29].

The presence of nickel has decreased the char gasification temperature by 100 °C. From a nickel concentration of 0.05 wt% in the impregnation solution equivalent at 0.38 wt% in the wood sample, Ni showed an important catalytic effect between 450 and 600 °C. These results reveal that in situ Ni^0 acts as the catalytic active phase for enhancing the syngas production. The validation of these results with the realization of gasification tests using phytoextraction plants could help to promote the valorization of those wastes at industrial scale.

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